



Influence of the oxide support reducibility on the CO₂ methanation over Ru-based catalysts



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ABSTRACT

Catalysts consisting of 5 wt.% ruthenium dispersed on four different metal oxide supports were synthesized with single-step flame spray pyrolysis and assessed for the hydrogenation of CO₂. The chosen supports covered a variety of characteristics expected to alter the catalytic performance, ranging from amphoteric and irreducible Al₂O₃, to amphoteric and reducible ZnO and MnO_x, to basic and reducible CeO₂. For the pristine metal oxide supports, the catalytic activity correlated with the oxide basicity and ZnO showed the highest CO₂ conversion. However, CO formation through the reverse water-gas shift reaction dominated over the CO₂ methanation due to a lack of H₂ dissociation sites. The addition of Ru created such H₂ dissociation sites and a significant increase in CO₂ conversion and CH₄ selectivity was observed. Combining the results of H₂ temperature-programmed reduction, quantitative H₂ and CO chemisorption, *in situ* DRIFTS, and the CO₂ hydrogenation reaction kinetics revealed that the Ru coverage with CO decreased with the support reducibility. For the irreducible Al₂O₃ support, the Ru particles were quasi-saturated with CO at low temperatures and the reaction was limited by the competitive Langmuir-type co-adsorption of H₂. The ZnO support lead to the lowest Ru-CO coverage associated with a weak CO adsorption and the reaction was dominated by the reverse water-gas shift reaction. CeO₂ showed a Ru-CO coverage in between Al₂O₃ and ZnO, which ensured the presence of H₂ dissociation sites while the Ru-CO adsorption strength remained sufficiently high.

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1. Introduction

Global warming due to excessive fossil fuel burning and the declining accessibility of such feedstock is fortifying the needs to secure clean and renewable energy resources [1–4]. Despite the advancement of photovoltaic and wind power technologies [5], their daily and seasonal intermittent availability remains a major obstacle, both in terms of constant energy supply and the associated infrastructures [6]. Large mismatch and fluctuations in the energy supply and demand necessitates the buffering by expensive electricity storage facilities. A promising alternative technology capable of compensating such fluctuations is the power-to-gas

(P2G) process, where excess electricity is converted to H₂ by electrolysis followed by the methanation of CO₂ (Sebastier reaction, CO₂ + 4H₂ → CH₄ + 2H₂O) [7–9]. The advantages of CO₂ methanation over direct H₂ or electricity storage are that CH₄ can be readily fed into the existing natural gas infrastructure and that the greenhouse gas CO₂ would become a recyclable chemical feedstock [10].

The most active and chemically stable catalysts hitherto reported for CO₂ methanation are those based on platinum group metals (e.g., Pt, Rh, Ru, Pd) [11–14]. The initial reaction step on such catalyst is the dissociative adsorption of CO₂ to form adsorbed CO and O (CO₂ → CO^{*} + O^{*}) [15–17]. The rate-limiting cleavage of the remaining C–O bond [17,18] can take place either by direct C–O dissociation to C^{*} and O^{*} [19–21], or through the H-assisted paths to form formyl or carbonyl hydride intermediates [16,17,22,23]. Further hydrogenation to CH_x and finally to CH₄ completes the catalytic cycle. Metal oxide supports such as Al₂O₃ [15,24–27], CeO₂ [12], TiO₂ [17,28], and SiO₂ [13,18,29] are commonly encountered in methanation catalysts but the understanding of metal-support interactions and their influence on the reaction mechanism is rarely

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straightforward. Depending on the type of support, its interaction with the supported metal can potentially modify the electronic state of the active sites, e.g., Ru/ZSM-5, resulting in a weakened Ru-CO bond [13]. The strength of the Ru-CO and Ru-H bonds directly dictates the surface coverage of the adsorbed reactants and hence the CH₄ selectivity [8,13]. At the same time, reactive sites on the supports such as the oxygen vacancies on CeO_{2-x} can directly dissociate CO₂ to CO* [12], while MgO can react with CO₂ to form MgCO₃ that serves as a reaction intermediate [29]. These active sites ought to be situated near the active metals where H₂ dissociation and spillover take place to catalyze the methanation of the support-dissociated CO₂.

In this paper, we aim to elucidate the effects of different metal oxide supports on the CO₂ methanation reaction mechanism of Ru-based catalysts. Here, the industrially-relevant flame spray pyrolysis (FSP) [30–33] is used to synthesize the supported Ru methanation catalysts. A number of metal oxide supports were included in the study, from strong Lewis acid [34] and irreducible Al₂O₃ to amphoteric and reducible CeO₂ and MnO_x as well as to strongly basic and reducible ZnO [34]. Through the combination of reaction kinetic studies and *in situ* diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS), the correlations between the support properties and the kinetics of CO₂ conversion as well as the products selectivities are reported. An in-depth understanding on the effect of supports is deemed necessary to allow better design of the CO₂ methanation catalysts by capitalizing on the potential synergistic metal-support interactions.

2. Experimental

2.1. One-step flame synthesis of CO₂ methanation catalysts

All catalysts were synthesized with a one-step flame spray pyrolysis reactor (FSP). Appropriate amounts of aluminum tri-sec-butoxide (97%, Acros), cerium(II) 2-ethylhexanoate (49% in 2-ethylhexanoic acid, Strem), manganese(II) 2-ethylhexanoate (40% in mineral spirit, Strem), and zinc(II) 2-ethylhexanoate (99%, Strem) were dissolved in a 20 vol.% acetonitrile (HPLC grade, Aldrich)/xylene (99%, Aldrich) mixture for a final metal concentration of 0.5 M. For the synthesis of Ru-containing catalyst, appropriate amounts of ruthenium acetylacetone (99%, Aldrich) were added to the solution for nominal loading of 5 wt.% Ru with respect to the products Al₂O₃, CeO₂, Mn₂O₃, and ZnO. A syringe pump delivered the precursor solution to the FSP nozzle with 5 mL min⁻¹ where it was dispersed with 5 L min⁻¹ O₂ (pressure drop at nozzle tip 1.5 bar). The precursor droplets were ignited by a supporting flame (1.5 L min⁻¹ CH₄ and 3.2 L min⁻¹ O₂) resulting in the primary aerosol-laden flame within which particles were formed. The particles were collected on a glassfiber filter (Whatmann GF/D, 25.7 cm) with the assistance of a vacuum pump.

2.2. Physicochemical characterization of CO₂ methanation catalysts

The temperature-programmed experiments were conducted on a Micromeritics AutoChem 2950 HP Chemisorption Analyzer connected to an external MicroStar 022 Mass Spectrometer. The catalyst was accurately weighed and placed into a quartz U-tube on top of a quartz wool plug. For the H₂ temperature-programmed reduction (H₂-TPR), 50 mg of sample were cooled to -80 °C under 50 mL min⁻¹ Ar followed by heating to 800 °C under 50 mL min⁻¹ 5% H₂/Ar with a temperature ramp of 10 °C min⁻¹. The CO₂ and H₂ temperature-programmed desorption (CO₂/H₂-TPD) and CO chemisorption were measured with 100 mg of catalyst after pretreatment with 50 mL min⁻¹ of 10% H₂/Ar for 1 h at 400 °C. For

the CO₂-TPD the sample was cooled to 25 °C under 50 mL min⁻¹ He followed by flushing with 50 mL min⁻¹ of 10% CO₂/He for 1 h. The gas stream was switched to 50 mL min⁻¹ of He for 30 min to remove weakly adsorbed CO₂ followed by heating to 800 °C at a temperature ramp of 10 °C min⁻¹. CO₂-TPDs of pristine supports were also measured but after a pretreatment with 50 mL min⁻¹ He since no reduction of RuO_x to Ru metal was required. For the H₂-TPD the sample was cooled to 25 °C under 50 mL min⁻¹ of 10% H₂/Ar followed by flushing with Ar at the same flowrate for 1 h to remove weakly adsorbed H₂. This was followed by heating to 800 °C at 10 °C min⁻¹. For the CO chemisorption, 50 mg of sample was cooled to -80 °C under flowing He followed by pulsing (loop volume 0.3194 mL) of 10% CO/He into the He carrier gas stream until no change in the CO peak areas was observed.

Diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted with a Tensor 27 (Bruker) equipped with a liquid N₂ cooled MCT detector and an *in situ* DRIFTS cell (Harrick Scientific). The average of 62 scans (corresponding to 30 s) is reported with a resolution of 8 cm⁻¹. The basic sites of the pristine supports were probed by pretreating the pristine supports with 200 mL min⁻¹ He at 350 °C for 10 min followed by cooling to 20 °C. Once the signal stabilized the background was recorded and 2 mL min⁻¹ CO₂ were introduced at t = 0. Spectra were collected every 30 s until no changes in the signal were observed. CO₂ adsorption on supported Ru samples were recorded with identical parameters but after a 10% H₂/He pretreatment. Once the CO₂ adsorption was completed, 6.4 mL min⁻¹ H₂ were added to the gas stream (λ of 0.8; see Eq. (2)). Next, the CO₂ flow was increased to 4 mL min⁻¹ (λ of 0.4) after which it was removed from the H₂/He flow. Again, spectra were recorded every 30 s to monitor the removal and hydrogenation of carbon species adsorbed on the catalyst.

The morphology of the catalysts was characterized with transmission electron microscopy (Philips CM-20). X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert3 at a scanning speed of 0.1° s⁻¹ and step size of 0.026° to identify the crystal structure of the samples. The instrument was equipped with a PIX-Cel 1D detector and the Cu K_α radiation was produced at 40 kV and 40 mA. The crystal phases were identified with X'Pert Highscore Plus.

2.3. Assessment of CO₂ methanation catalysts

All catalytic experiments were conducted in a quartz tube fix bed reactor (I.D. = 5 mm, GHSV = 7640 h⁻¹) containing 20 mg of as-synthesized catalyst diluted in 0.4 g silicon carbide (Aldrich, 200–450 mesh particle size). The sample was pretreated at 400 °C for 1 h with 50 mL min⁻¹ of 10% H₂/Ar. A K-type thermocouple was inserted into the center of the catalyst bed to monitor the reaction temperature. The gas outlet composition was measured with two online gas chromatographs (GC8A, Shimadzu) connected in series, one equipped with a flame ionization detector (FID) and another with a temperature conductivity detector (TCD). Calibrated mass flow controllers (Aalborg and Bronkhorst) at the reactor inlet delivered the gas flows of H₂, CO₂ and Ar for an overall flow rate of 50 mL min⁻¹. The CH₄ selectivity was defined as:

$$S(\%) = \frac{CH_{4,out}}{CH_{4,out} + CO_{out}} \quad (1)$$

where CH_{4,out} and CO_{out} are the CH₄ and CO concentrations at the reactor outlet, respectively. The ratio between H₂ and CO₂ was defined as:

$$\lambda = \frac{H_{2,in}}{4 \cdot CO_{2,in}} \quad (2)$$

Table 1

Applied space groups and bulk lattice constants of the simulated MnO₂ [40], Al₂O₃ [41], CeO₂ [42], ZnO [43], and Ru [44]. Also shown are the parameters of the modeled metal oxide support surface.

Metal oxide	Space group	a	b	c	Modeled surface	Surface dimension	Layer thickness
–	–	Å	Å	Å	–	Å	Å
MnO ₂	P4/mnm	4.40	4.40	2.87	(110)-(4 × 2)	11.5 × 12.4	8.7
Al ₂ O ₃	P2 ₁ /m	5.59	8.41	8.07	(100)- $\sqrt{2} \times \sqrt{2}$	11.7 × 11.7	8.6
CeO ₂	Fm-3m	5.41	5.41	5.41	(111)- $(2\sqrt{2} \times 3\sqrt{2})$	13.3 × 11.5	7.8
ZnO	P6 ₃ mc	3.25	3.25	5.21	(0001)- $(4\sqrt{2} \times 2\sqrt{2})$	13.0 × 11.3	8.4
Ru	P6 ₃ /mmc	2.71	2.71	4.28	–	–	–

based on the stoichiometry of the Sabatier reaction (CO₂ + 4H₂ → CH₄ + 2H₂O), where H_{2,in} and CO_{2,in} are the inlet concentrations of H₂ and CO₂, respectively. The CO₂ conversion and CH₄ selectivity were assessed between 250 and 700 °C. The CO₂ conversion hereby directly reflects the reaction rate in mol_{CO₂} g_{Ru}⁻¹ s⁻¹ due to the constant Ru loading. To assure that the reaction was not limited by thermodynamics, additional measurements at 200 °C were conducted and used for calculating the activation energies.

2.4. Density-functional theory (DFT) calculations

Density functional theory (DFT) [35,36] was used to study the interaction between the reaction gases CO₂/H₂/CO and the supported Ru clusters. The space groups, lattice constants, modeled surface and its dimensions, and the layer thickness of the considered metal oxide supports are listed in Table 1. A Ru₁₉ cluster with an initial top surface orientation (0001) was constructed from the hexagonal Ru bulk structure and placed on the different oxide supports. Structural optimization led to stable Ru nanoparticles in the same size range as observed experimentally and with a variety of Ru edge and corner atoms. A vacuum gap of 15 Å was used to avoid interactions between periodic images.

All DFT calculations were carried out using the QUANTUM ESPRESSO package [37]. Spin-polarized calculations were conducted using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [38], and the ultra-soft pseudopotentials [39]. The plane wave basis sets with the kinetic energy cutoffs of 25 and 200 Ry were used for the wave functions and augmented charge density, respectively. Gamma point sampling of the reciprocal space is adequate for this system due to the large size of the supercell.

3. Results and discussion

3.1. Catalyst synthesis and physiochemical characterization

The direct flame spray pyrolysis (FSP) of co-dissolved ruthenium acetylacetone and the metal oxide support precursors resulted in nanoparticles of necked spherical Ru/MnO_x aggregates, spherical Ru/Al₂O₃, rhombohedral Ru/CeO₂ and rod-shaped Ru/ZnO (Fig. 1). The morphologies of these Ru-loaded particles are consistent with previous work on pristine oxides synthesized with the FSP [45–51]. XRD measurements revealed the formation of CeO₂, γ-Al₂O₃, and a mixture of Mn₂O₃ and Mn₃O₄ (Fig. S1), in agreement with literature reports of these flame-made oxides [52,53]. No Ru diffraction peaks

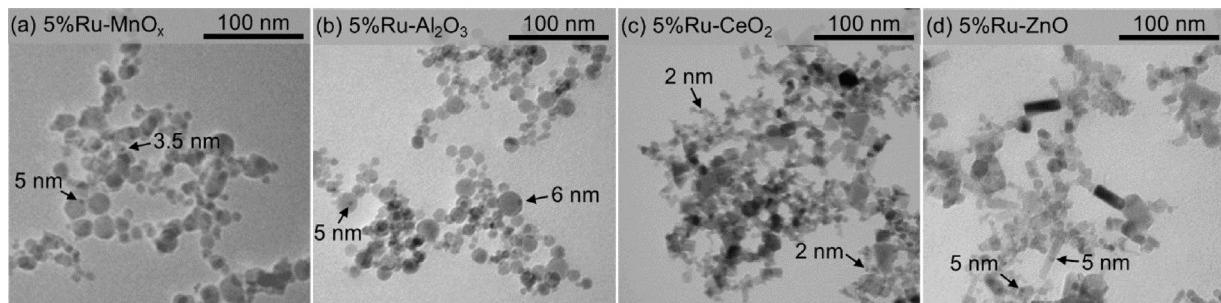


Fig. 1. TEM images of the as-synthesized (a) Ru/MnO_x, (b) Ru/Al₂O₃, (c) Ru/CeO₂ and (d) Ru/ZnO. The arrows indicate possible Ru particles on the respective oxide support.

Table 2

Quantification of H₂ consumed during H₂-TPRs, CO₂ desorbed during CO₂-TPDs, amount of CO adsorbed during CO pulsed chemisorption, and H₂ desorbed during H₂-TPDs. Also shown are the estimated Ru particle sizes based on the amount of adsorbed H₂.

Catalyst ^a	H ₂ consumed during TPR ^b	Theor. H ₂ consumption RuO ₂ → Ru	CO ₂ desorbed during TPD ^c	CO chemisorbed ^d CO _{ad}	H chemisorbed ^{d,e} H _{ad}	d _{Ru} ^f	H _{ad} /CO _{ad}
	mmol _{H2} g ⁻¹	mmol _{H2} g ⁻¹	mmol _{CO2} g ⁻¹	mmol _{CO} g ⁻¹	mmol _H g ⁻¹	nm	–
Ru/MnO _x	5.11		0.56	0.04	0.39	1.7	10.8
Ru/Al ₂ O ₃	0.73		0.23	0.11	0.09	7.1	0.83
Ru/CeO ₂	2.75	0.99	1.25	0.12	0.42	1.6	3.4
Ru/ZnO	1.17		0.34	0.01	0.11	5.8	12.6

^a 5 wt.% nominal Ru loading with respect to the support.

^b Quantified by integrating the H₂-TPR peaks in Fig. 2.

^c Quantified by integrating the CO₂-TPD peaks in Fig. 3.

^d Measured through CO pulsed chemisorption after pre-reduction of catalyst with 10% H₂/Ar at 400 °C for 1 h.

^e Estimated from integrating the peaks during H₂-TPD.

^f Calculated from H_{ad} assuming hemispherical particle shape and Ru:H of 1.0.

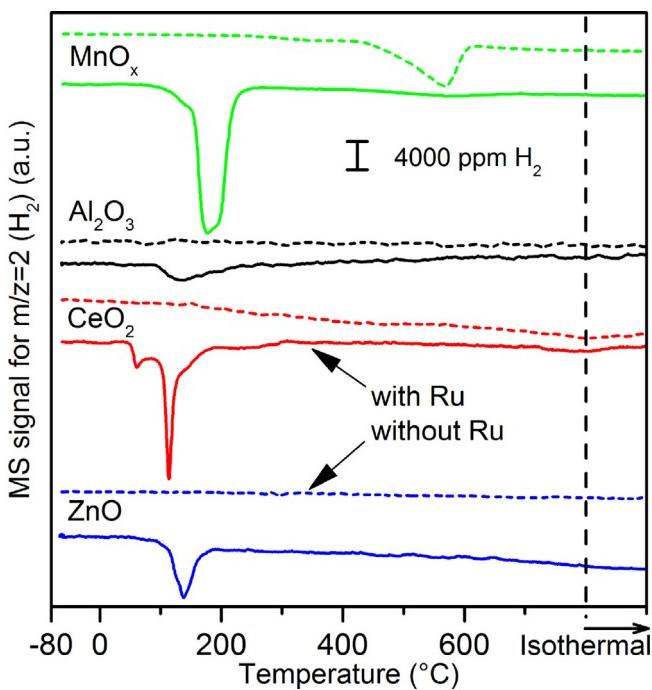


Fig. 2. H₂ temperature-programmed reduction of the pristine metal oxides (dotted lines) and the catalysts consisting of 5% Ru supported on the respective oxides (solid lines).

were observed, in agreement with the 5 wt.% Ru loading and the small particle size deduced from the chemisorption studies (see below). The dark spots in the range of 2–6 nm (Fig. 1) might indicate Ru clusters but unambiguous identification and sizing of Ru with TEM was not possible. Gas adsorption will be discussed below as a more accurate and reliable technique to measure the Ru particle size.

Fig. 2 shows the characterization of the catalyst with H₂ temperature-programmed reduction (H₂-TPR). No reduction peak can be seen for the less reducible pristine supports, i.e., ZnO and Al₂O₃, but upon the addition of Ru, a prominent reduction peak in between 100 and 200 °C emerged. To some extent, this low-temperature peak can be explained by the reduction of RuO_x to Ru metal. However, the H₂ consumption was higher than that expected for the stoichiometric reduction of RuO₂ to Ru⁰ (Table 2) indicating partial support reduction due to H-spillover. An exception is the Ru/Al₂O₃ catalyst as can be expected for the irreducible Al₂O₃. For the highly reducible supports CeO₂ and MnO_x, the amount of H₂ consumption was 2.8 and 5.1 times that required for the stoichiometric RuO₂ → Ru. The two-step reduction of Ru/CeO₂ can be explained by reduction of the facets of the CeO₂ rhombohedra [54–56].

The quantitative CO₂ temperature-programmed desorption (CO₂-TPD) was performed on the catalysts to measure the number of basic surface sites and their strength of basicity (Fig. 3) [57,58]. In general, only minor differences in the TPD profiles can be seen between the pristine (dotted lines) and Ru-loaded supports (solid lines) indicating that most CO₂ adsorption sites exist on the oxide supports. The Ru/ZnO catalyst contains the strongest basic sites with CO₂ desorption observed at 450 °C in agreement with the strong basicity reported for ZnO [34]. These basic sites typically react with the CO₂ to form carbonates and formates, which speciation will be confirmed below using the DRIFTS. Despite the strength of the ZnO basicity, the amount of sites is moderate (0.34 mmol g⁻¹), compared to Ru/CeO₂ (1.25 mmol g⁻¹) which is known to be a basic support [34]. Even though oxygen vacancies can be expected in the Ru/CeO₂ catalyst after the H₂ pretreatment

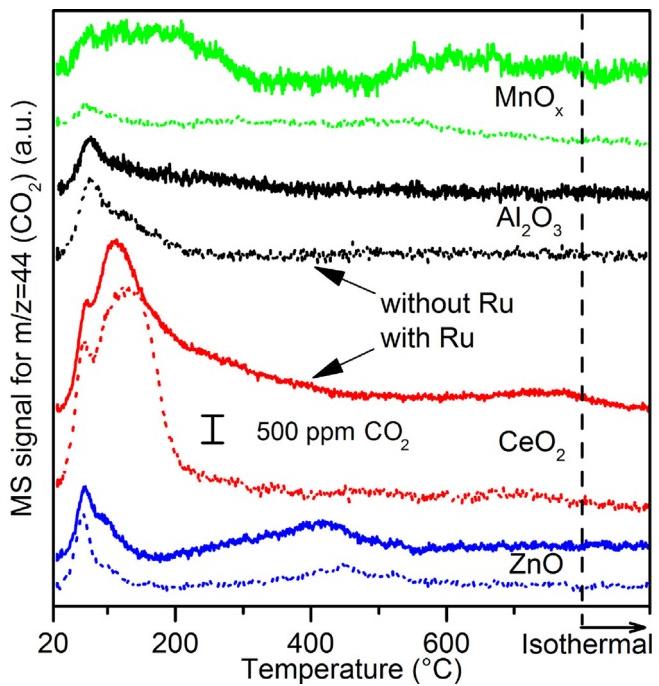


Fig. 3. CO₂ temperature-programmed desorption of the pristine metal oxides (dotted lines) and the catalysts consisting of 5% Ru supported on the respective metal oxides (solid lines).

(1 h at 400 °C; Fig. 2), the absence of CO desorption suggests that CO₂ adsorption on CeO₂ vacancies was limited [59]. Only moderate CO₂ desorption from the Ru/Al₂O₃ (0.23 mmol g⁻¹) and Ru/MnO_x (0.56 mmol g⁻¹) sample was detected indicating little CO₂ adsorption on weak basic sites.

The mode of CO₂ adsorption on the supports was determined with DRIFTS (Fig. 4). The CO₂ adsorption on the Al₂O₃ surface shows the characteristics of bridged bicarbonates as reflected from the O—C—O symmetric (1434 cm⁻¹) and antisymmetric (1655 cm⁻¹) stretching peaks, as well as the O—H stretching at 3624 cm⁻¹ and C—O—H deformation at 1228 cm⁻¹ [60,61]. The bicarbonate species on these weak basic sites of Al₂O₃ were formed with the surface hydroxyl groups on Al₂O₃ left after the He pretreatment as indicated by the emerging valley in the OH stretching region (3762 cm⁻¹; Fig. 4b) [16,60]. The broad peaks in the C—O vibrational region with peak positions around 1640, 1350–1380, and 1010–1040 cm⁻¹ are likely due to the additional presence of mono- and bidentate carbonates on Al₂O₃ [60,62]. The analogous bridged bicarbonate peaks of CeO₂ are located at 3621, 1650, 1408, 1216 cm⁻¹ along with OH consumption at 3686 cm⁻¹ (Fig. 4c) [63]. The peaks at 1625, 1245, 1014, and 851 cm⁻¹ are assigned to bidentate carbonate while the smaller peaks at 1533, 1339, 1058 cm⁻¹ are attributed to monodentate carbonate. The former is mainly accountable for the low temperature CO₂-TPD peaks at 68 and 112 °C, while the more stable structure of the latter is likely to be responsible for the tailing up to 400 °C [64,65]. Bridged bicarbonate peaks on MnO_x were observed at 1639, 1408, and 1274 cm⁻¹ (Fig. 4a). Furthermore, the C—H stretching at 2929 and 2858 cm⁻¹ combined with the peaks at 1543 and 1370 cm⁻¹ suggest the formation of bidentate or bridged formates [63,66]. The adsorption of CO₂ on ZnO resulted in significant amounts of bicarbonate and formate formation as can be seen in the C—O—H and C—H regions at 3730–3510 and 2970–2850 cm⁻¹, respectively (Fig. 4d). Precise peaks assignment in the C—O vibrational region in case of ZnO is difficult due to the large number of overlapping peaks (Fig. 4d).

The adsorbed H₂ on the Ru surface was quantified by the H₂-TPD. As tabulated in Table 2, the highest amount of chemisorbed H₂

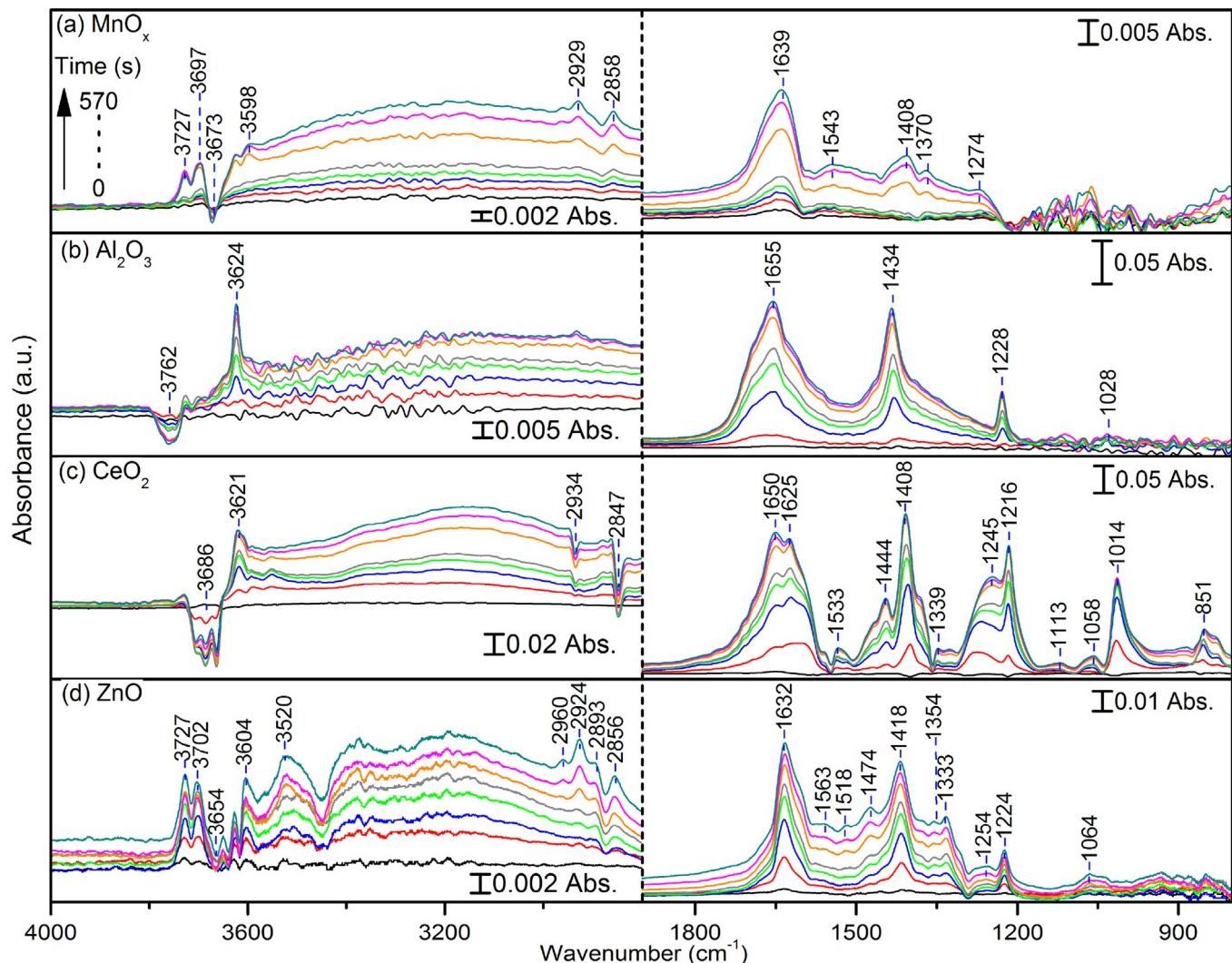


Fig. 4. Time-resolved DRIFT spectra in the C—H/C—O (4000–2800 cm⁻¹) and C—O vibrational range (1900–800 cm⁻¹) of pristine metal oxides of (a) MnO_x, (b) Al₂O₃, (c) CeO₂ and (d) ZnO, upon the introduction of 1% CO₂/He at 20 °C.

was measured for the Ru/CeO₂ sample (0.42 mmol g⁻¹) followed by Ru/MnO_x (0.39 mmol g⁻¹), Ru/ZnO (0.11 mmol g⁻¹) and Ru/Al₂O₃ (0.09 mmol g⁻¹). Assuming a ratio of chemisorbed H atom to surface Ru atom of 1:1 [67], the corresponding Ru particle sizes are 1.6, 1.7, 5.8, and 7.1 nm, respectively. The calculated Ru sizes are in good qualitative agreement with the small Ru particles observed under TEM (Fig. 1) and absence of Ru peaks in the XRD (Fig. S1). CO

chemisorption was applied as an alternative technique to determine the Ru particle size (Table 2). The amount of CO chemisorbed on Ru/Al₂O₃ was slightly larger than that of H₂, possibly due to carbonyl formation [68]. For the other samples however the amount of adsorbed CO was significantly lower and H_{ad}/CO_{ad} ratios of 3.4–12.6 were calculated (Table 2). A change in the number of exposed Ru sites would equally shift H_{ad} and CO_{ad} and can thus not explain the

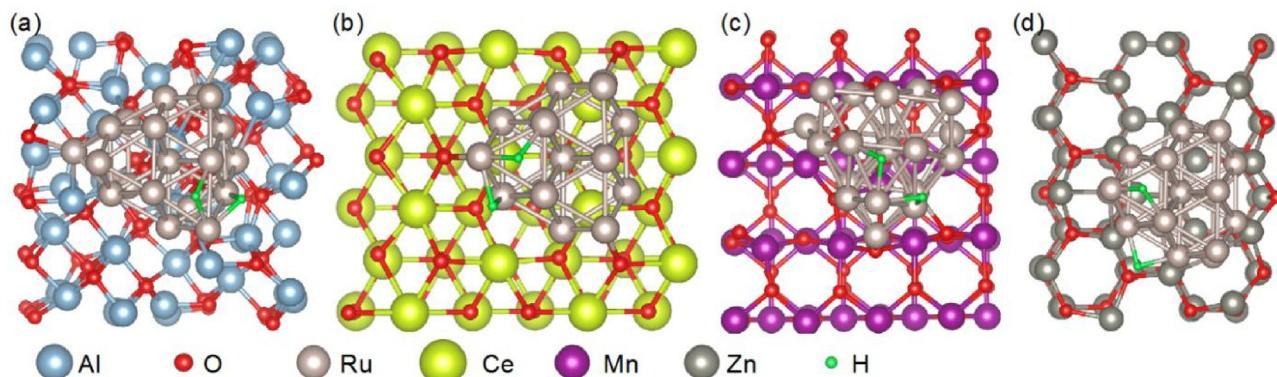


Fig. 5. Dissociative H₂ adsorption to the Ru cluster supported on (a) Al₂O₃, (b) CeO₂, (c) MnO_x, and (d) ZnO.

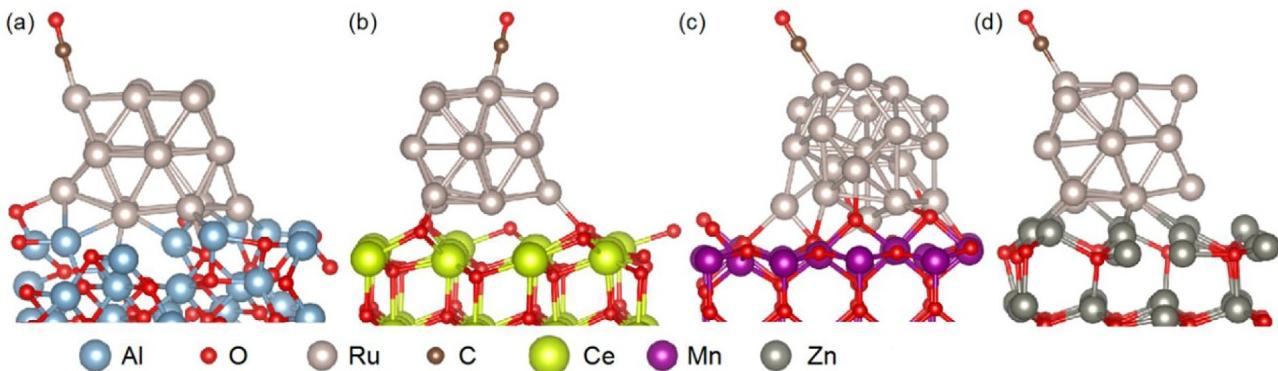


Fig. 6. CO adsorption to the Ru cluster supported on (a) Al_2O_3 , (b) CeO_2 , (c) MnO_2 , and (d) ZnO .

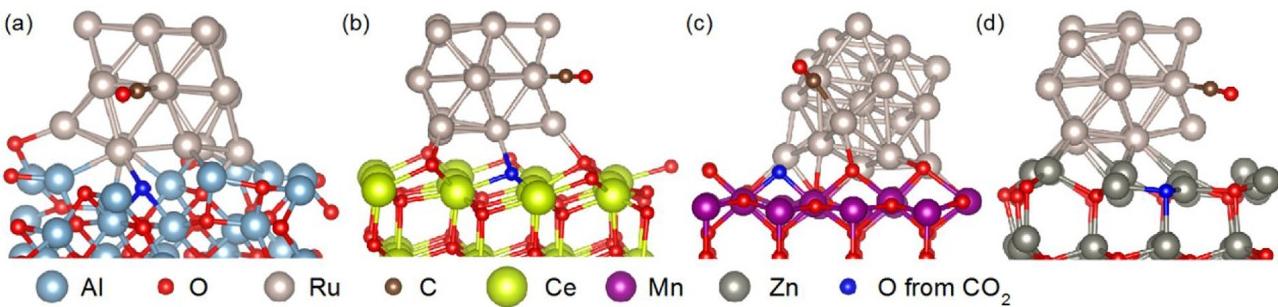


Fig. 7. Dissociative CO_2 adsorption to the Ru cluster supported on (a) Al_2O_3 , (b) CeO_2 , (c) MnO_2 , and (d) ZnO . The CO is on the Ru cluster and the O is in the vacancy on the oxide surface.

Table 3

Energies of H_2 dissociative adsorption, CO adsorption and CO_2 dissociative adsorption to the Ru cluster supported on Al_2O_3 , CeO_2 , MnO_2 , and ZnO .

Catalyst ^a	H_2	CO	CO_2
	kcal/mol	kcal/mol	kcal/mol
Ru/ MnO_x	-20.9	-50.5	-78.8
Ru/ Al_2O_3	-24.3	-50.6	-62.5
Ru/ CeO_2	-22.3	-49.8	-23.9
Ru/ ZnO	-25.6	-51.3	-52.0

^a 5 wt.% nominal Ru loading with respect to the support.

differences in the $\text{H}_{\text{ad}}/\text{CO}_{\text{ad}}$ ratio. Interestingly, the $\text{H}_{\text{ad}}/\text{CO}_{\text{ad}}$ ratios are in the sequence $\text{Ru}/\text{Al}_2\text{O}_3 < \text{Ru}/\text{CeO}_2 < \text{Ru}/\text{MnO}_x$ and therefore follow the same order as the amount of H_2 consumed during H_2 -TPR. A decrease in the amount of CO adsorption on precious metals was reported to originate from a decreased electron density in the metal d -band upon H_2 reduction of the support. Due to the decreased density, the electron back-donation from the metal d -band to the π^* anti-orbital of CO is reduced, leading to a weaker CO adsorption [69,70]. The high $\text{H}_{\text{ad}}/\text{CO}_{\text{ad}}$ ratio of 12.6 calculated for the Ru/ZnO sample might therefore be caused by a more pronounced weakening of the CO on Ru adsorption due to the two electron reduction of Zn^{2+} to Zn^0 during the H_2 pretreatment.

Density functional calculations were performed to study H_2 and CO adsorption on the Ru clusters. Fig. 5 and Fig. 6 show, respectively, the adsorption structures of H_2 and CO on Ru/ Al_2O_3 , Ru/ CeO_2 , Ru/ MnO_2 and Ru/ ZnO . As consistent with the experimental results, the calculated negative adsorption energies indicate that it is energetically favorable for the H_2 to adsorb dissociatively. The formed chemisorbed H^* was shown to be a key intermediate in the CO_2 hydrogenation mechanism [16,18]. The H_2 and CO adsorption energies on Ru/ Al_2O_3 , Ru/ CeO_2 , Ru/ MnO_2 and Ru/ ZnO are listed in Table 3. Across different metal oxide supports, the CO was consistently found to adsorb significantly stronger than the H_2 . This

adsorption strength difference is a key factor in determining the CO_2 methanation rate on the Ru cluster with different metal oxide supports as will be discussed in Section 3.4. A more detailed DFT study would be required to confirm the reported decreased electron density in the metal d -band upon reduction of the support [69,70], which is beyond the scope of this work.

As CO_2 dissociation is required prior CO adsorption on Ru, DFT calculations of this process were also performed. We found that the dissociative CO_2 adsorption might involve one O of the CO_2 interacting with a metal oxide surface vacancy close to the Ru cluster while the CO remains on the Ru surface (Fig. 7). In the subsequent reaction steps, the hereby formed chemisorbed CO^* hydrogenates with co-adsorbed H^* as will be discussed in section 3.4.

3.2. Catalytic methanation of CO_2

The CO_2 conversion and CH_4 selectivity of the pristine supports and Ru containing samples are shown in Fig. 8. Notably, the trend of CO_2 conversion over the pristine supports follows the strength of the support basicity as determined with CO_2 -TPD, that is, $\text{ZnO} > \text{CeO}_2 > \text{MnO}_x > \text{Al}_2\text{O}_3$ (Fig. 3). The ZnO sample with its strong basic sites was the most active sample and even reached the thermodynamic equilibrium limit at 600°C (Fig. 8a). Pristine CeO_2 approaches the thermodynamic conversion at 700°C , while MnO_x and Al_2O_3 only exhibited less than 20% CO_2 conversion even at 700°C . At these high temperatures, the products are mainly CO as the reverse water-gas shift reaction (RWGS; $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) dominates (Fig. 8b). The addition of Ru allows the activation of the catalysts at lower temperatures and for the CH_4 formation. The CO_2 conversion and CH_4 selectivity followed the order of $\text{Ru}/\text{CeO}_2 > \text{Ru}/\text{Al}_2\text{O}_3 > \text{Ru}/\text{MnO}_x > \text{Ru}/\text{ZnO}$. These samples approached the thermodynamic conversion at 350, 400, 450 and 500°C (Fig. 8). High CH_4 selectivities (> 90%) can be obtained for the three most active catalysts at 350°C , beyond which the RWGS

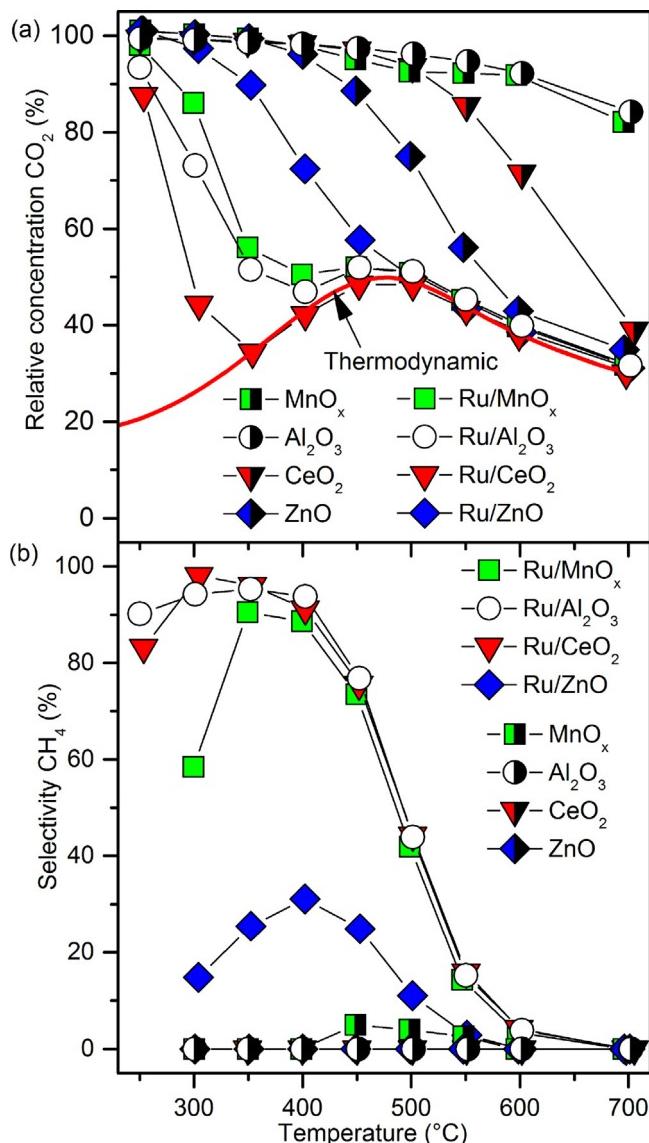


Fig. 8. (a) Relative CO₂ concentration and (b) CH₄ selectivity over pristine metal oxides and the catalysts consisting of 5% Ru supported on the respective metal oxides. Shown as red solid line is the thermodynamic equilibrium level calculated by minimizing the Gibbs free energy. Reactants: 2.3% CO₂, 7.4% H₂, balance in Ar, equivalence ratio, $\lambda = 0.8$; GHSV: 7640 h⁻¹. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

favoring the CO production becomes significant. It is interesting to note that the CO₂ conversions are in qualitative agreement with the trend of CO chemisorption (see Table 2).

The Arrhenius plot in Fig. 9 reveals relatively similar apparent activation energy values, E_a , between Ru/CeO₂ (75 ± 2 kJ mol⁻¹), Ru/Al₂O₃ (77 ± 2 kJ mol⁻¹), and Ru/MnO_x (84 ± 3 kJ mol⁻¹). These are well within the reported values of 72–105 kJ mol⁻¹ for the CO₂ methanation over supported Ru catalysts [20,71]. Furthermore, the values are comparable to the activation energy of CO methanation, suggesting that the initial CO₂ dissociation is not the limiting step [17,18]. The relatively high E_a of 108 ± 3 kJ mol⁻¹ for Ru/ZnO is probably a reflection of the dominant RWGS that resulted in a low CH₄ selectivity (Fig. 8b). As tabulated in Table 4, the turnover frequency (TOF) is the highest for Ru/Al₂O₃ ($38 \cdot 10^{-2}$ s⁻¹) followed by Ru/CeO₂ ($15 \cdot 10^{-2}$ s⁻¹), Ru/ZnO ($6 \cdot 10^{-2}$ s⁻¹) and Ru/MnO_x ($5 \cdot 10^{-2}$ s⁻¹) at 300 °C and with excess H₂ ($\lambda = 1.2$). The different TOFs corroborate the notion of a non-negligible effect of the metal oxide supports.

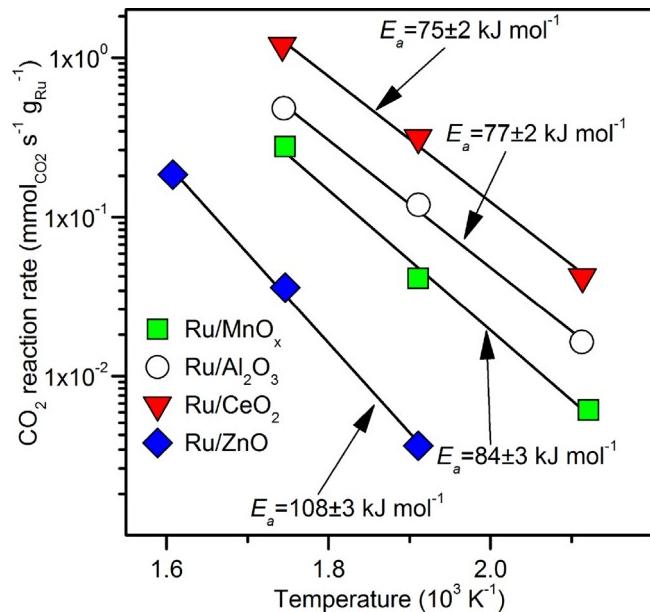


Fig. 9. Arrhenius plot of Ru/MnO_x, Ru/Al₂O₃, Ru/CeO₂ and Ru/ZnO, and the corresponding apparent activation energies, E_a , in kJ mol⁻¹.

Table 4

Turnover frequencies (TOFs) with the corresponding CO₂ conversion and CH₄ selectivity based on the rates of CO₂ consumption and CH₄/CO production.

Catalyst ^a	CO ₂ conv. %	CH ₄ selectivity %	TOF _{CO2} ^b	TOF _{CH4} ^b	TOF _{CO} ^b
			10 ⁻² , s ⁻¹	10 ⁻² , s ⁻¹	10 ⁻² , s ⁻¹
Ru/MnO _x	25	90	5	5	0.5
Ru/Al ₂ O ₃	32	94	38	36	2
Ru/CeO ₂	83	99	15	15	0.1
Ru/ZnO	1	6	6	0.4	6

^a Reactor bed = 20 mg catalyst diluted in 0.4 g silicon carbide, GHSV = 7640 h⁻¹, 22% H₂, 4.6% CO₂, balance in Ar, reaction temperature = 300 °C.

^b Turnover frequency (TOF) calculated based on the steady state rate of CO₂ conversion, CH₄ production or CO production, and the dispersion of Ru as measured from H₂-TPD.

Additional catalytic experiments were conducted as a function of H₂ (Fig. 10) and CO₂ concentration (Fig. 11). The increase in the equivalence ratio, ($\lambda = [\text{H}_2]/[4[\text{CO}_2]]$), increases the CO₂ conversion for all catalysts (Fig. 10a), as also predicted thermodynamically. More importantly, Ru/MnO_x, Ru/Al₂O₃ and Ru/CeO₂ were able to attain the equilibrium conversions from relatively low temperatures of ~300 °C (Fig. 10a). Maximum CH₄ production rates were measured for these catalysts at 350 °C (Fig. 10b), coinciding with the onset of the endothermic RWGS reaction, after which CO production increases with increasing temperatures (Fig. 10c). The actual production rates of CH₄ and CO are well within the thermodynamic prediction for these three catalysts, which exhibit similar E_a . Intriguingly, the Ru/ZnO favors RWGS over CO₂ methanation even at the lower temperatures where the latter is expected to be dominant (Fig. 10c and Fig. 11c). This becomes evident from the higher rates of CO production than that predicted at theoretical equilibrium, at the expense of the low CH₄ production rates.

The dependencies of CH₄ production rates on H₂ and CO₂ concentrations can be better reflected from the respective log-log plots measured at sub-equilibrium levels (Fig. 12). A first order reaction with respect to the H₂ concentration was measured for all supported Ru catalysts, except for Ru/Al₂O₃ (0.7 ± 0.05 ; Fig. 12a). The first order dependency is consistent with the expected rate determining step of CO* hydrogenation [17,18]. The lower reaction order for Ru/Al₂O₃ is likely caused by a quasi-saturation of

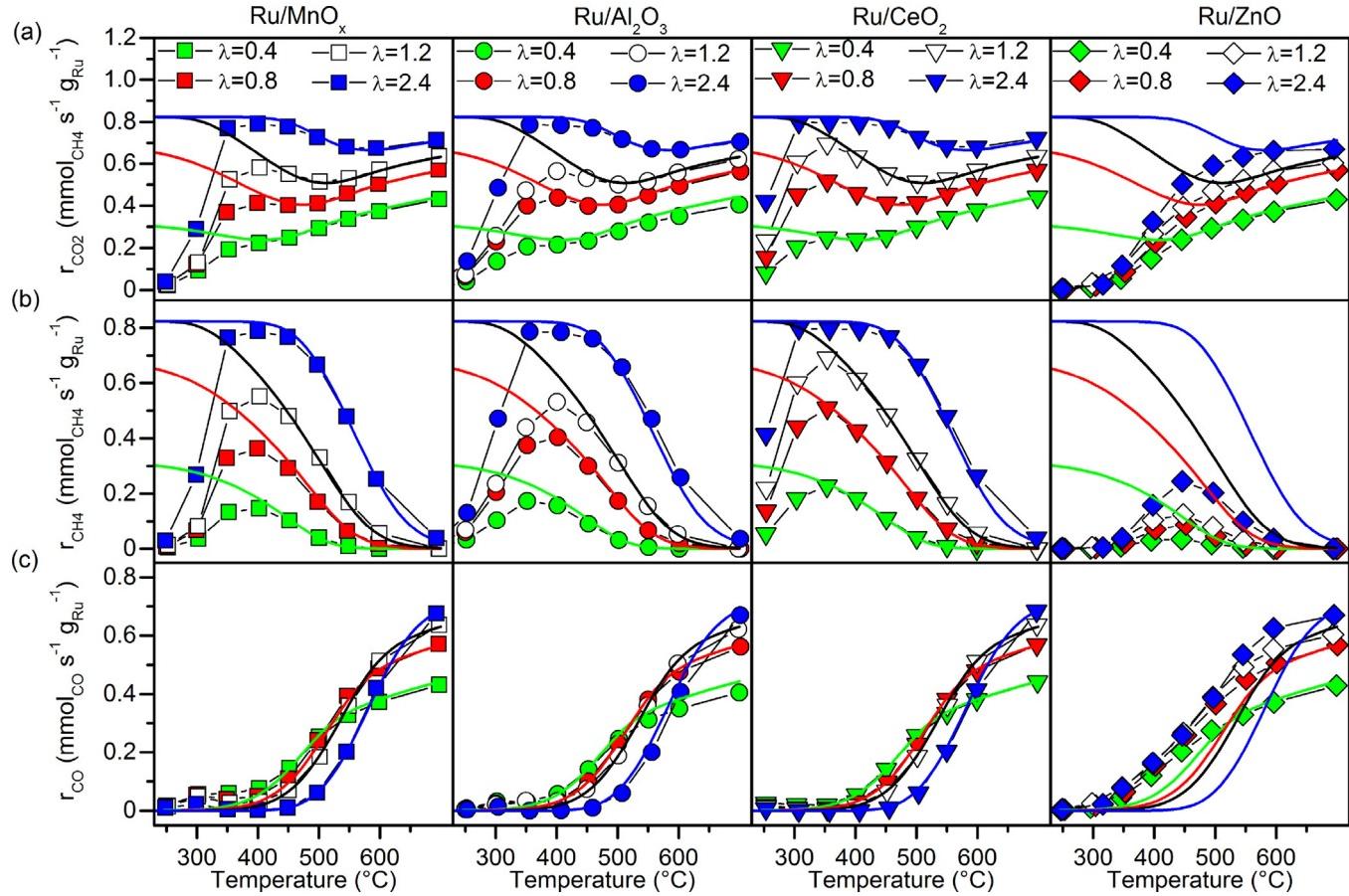


Fig. 10. The steady state rates of (a) CO₂ conversion, (b) CH₄ production and (c) CO production measured as a function of the equivalence ratios, λ , of 0.4, 0.8, 1.2 and 2.4 with a constant CO₂ reactant concentration of 2.3%. Shown in solid lines are the thermodynamic equilibrium levels calculated by minimizing the Gibbs free energy.

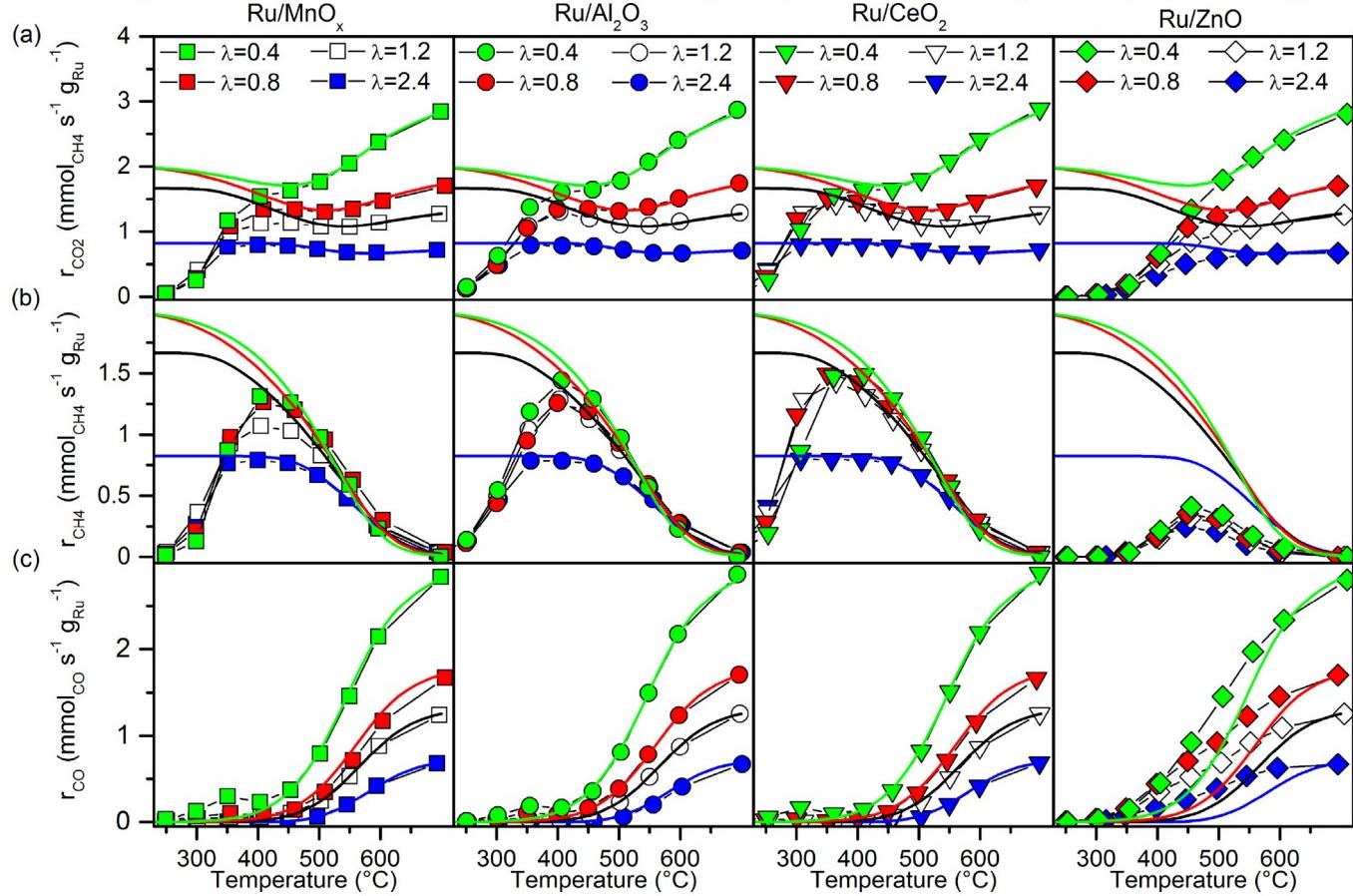


Fig. 11. The steady state rates of (a) CO₂ conversion, (b) CH₄ production and (c) CO production rates measured as a function of the equivalence ratios, λ ,

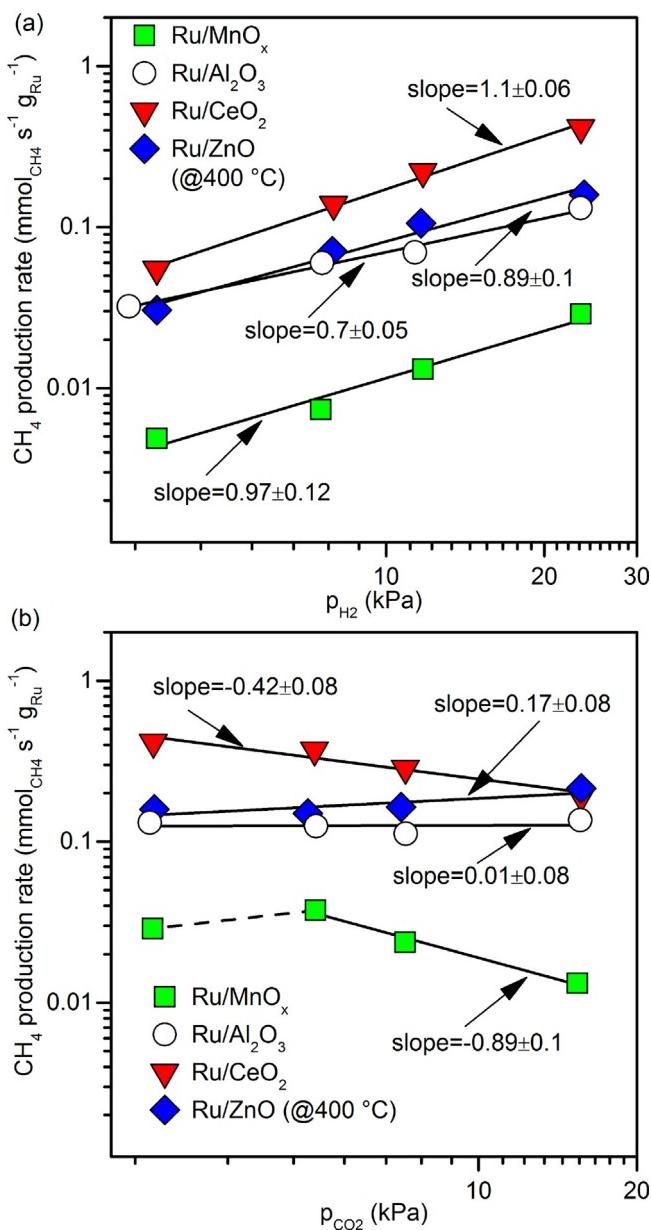


Fig. 12. The rates of methane production measured as a function of (a) H₂ and (b) CO₂ partial pressures over Ru/MnO_x, Ru/Al₂O₃, Ru/CeO₂ and Ru/ZnO. The reaction temperature was 250 °C except for Ru/ZnO which was 400 °C due to low catalytic conversions.

Ru by CO due to the stronger Ru-CO adsorption in case of irreducible supports. This would limit the sites for H₂ dissociation and thus reduce the influence of the H₂ partial pressure on the CH₄ production rate. As shown in Fig. 12b, the dependency of CH₄ production rates on CO₂ concentration is more complex. The order of reaction with respect to CO₂ ranges from slightly positive for Ru/ZnO (0.17 ± 0.08) to zero for Ru/Al₂O₃ (0.01 ± 0.08) and negative for Ru/CeO₂ (-0.42 ± 0.08) and Ru/MnO_x (-0.89 ± 0.1). The difference can be traced to the competitive Langmuir-type adsorption of the key intermediates CO* and H* on Ru as function of support reducibility (see H_{ad}/CO_{ad} ratios in Table 2). The Ru/Al₂O₃ catalyst is expected to be quasi-saturated with CO even at low CO₂ concentration due to the strong Ru-CO adsorption in case of irreducible

supports. Therefore, a change in CO₂ partial pressure has no effect on the CH₄ production rate and a zero reaction order is observed. For the reducible supports CeO₂ and MnO_x, a larger number of H₂ dissociation sites are available which are however lost at higher CO₂ concentrations as reflected by the negative CO₂ reaction order. For the Ru/ZnO catalyst, barely any CO adsorbs on Ru and larger CO₂ concentrations are required to obtain appreciable amounts of CO*.

3.3. *in situ* DRIFTS of catalytic CO₂ methanation

In situ DRIFTS were carried out to follow the speciation on the catalysts under reaction environment. Comparing the spectra of the as-synthesized and pretreated samples shows absorption peak around 2130–1780 cm⁻¹ (Fig. S2). This peak only develops after H₂ was introduced at elevated temperatures and disappears upon exposing the sample to air, suggesting that it may be related to the Ru-O overtone of some RuO_x–OH species [72,73]. A drastic decrease in the IR after the reduction of Ru/ZnO prevented acquisition of IR absorbance signal (Fig. S2d). Instead, the Ru/ZnO was only treated under He at the same temperature to remove any moisture and organic/carbonate impurities from the surface. The subsequent cooling of the catalyst to 250 °C and the introduction of 1% CO₂ saw the formation of bridged carbonates on Ru/Al₂O₃ with peaks at 3619, 1647, 1444, and 1231 cm⁻¹ (Fig. 13b) [60,61]. Additionally, a peak for the carbonyl on Ru can be seen at 2066 cm⁻¹ as well as significant amounts of C–H bonds (see 2926 and 2857 cm⁻¹ at t=0 in Fig. 14b). The surface carbonyl reflects the dissociative adsorption of CO₂ leading to CO on Ru, and the intensity scales qualitatively with the amount of chemisorbed CO seen earlier from the pulsed CO chemisorption (Table 2). The formed C–H bonds, combined with the peaks at 1539 and 1331 cm⁻¹, can be assigned to bidentate formates, which are formed from the carbonation of the surface hydroxyl moieties [63,66]. The formation of formates were also recorded for Ru/CeO₂ (Fig. 13c) and Ru/MnO_x (Fig. 13a). In both cases, the peaks at around 850 cm⁻¹ can be assigned to mono- or bidentate carbonates. As the Ru/ZnO sample was not reduced, only negligible amount of carbonyl on Ru can be detected at 2026 cm⁻¹.

Subsequent co-introduction of H₂ resulted in the catalyst reduction as seen by the decreasing valley at 2130–1780 cm⁻¹ (Fig. 14a–c). The hydroxyl groups consumed during CO₂ adsorption to form formates are regenerated and an increase in the C–H vibrational peak can be observed. Accordingly, C–O vibrational peaks assigned to formate species increase (Fig. 14a–c). A red shift in the IR absorbance peaks of carbonyl on Ru from 2065 cm⁻¹ for Ru/Al₂O₃ to 2057 cm⁻¹ for Ru/CeO₂ and 2045 cm⁻¹ for Ru/MnO_x can be observed (Fig. 14d). A red shift of the carbonyl peak was reported to be caused by decreasing coverage of CO on precious metals and the accompanied decrease of the dipole–dipole coupling of co-adsorbed CO molecules [74]. The expected H*/CO* surface coverage of Ru based on the measured H_{ad}/CO_{ad} ratio (Table 2) agrees well with a decreasing CO coverage from Ru/Al₂O₃ to Ru/CeO₂ to Ru/MnO_x. Removing CO₂ from the CO₂/H₂/He gas mixture resulted in a gradual decrease of the carbonyl and carbonate/formate peaks (Fig. 15). Notably, the C–H peaks around 3000–2700 cm⁻¹ remains almost unchanged. Most likely the C–H stretching peak is not only caused by the formate species but overlaps with adsorbed CH₂ or CH₃ [16]. Addition of CO₂ into a H₂/He gas stream (Fig. S3) resulted in qualitatively similar DRIFTS peaks as H₂ addition to a CO₂ stream (Fig. 14), indicating that the sequence of introduced reactants has little influence on the formed intermediates/products.

of 0.4, 0.8, 1.2 and 2.4 and a constant H₂ reactant concentration of 22%. Shown in solid lines are the thermodynamic equilibrium levels calculated by minimizing the Gibbs free energy.

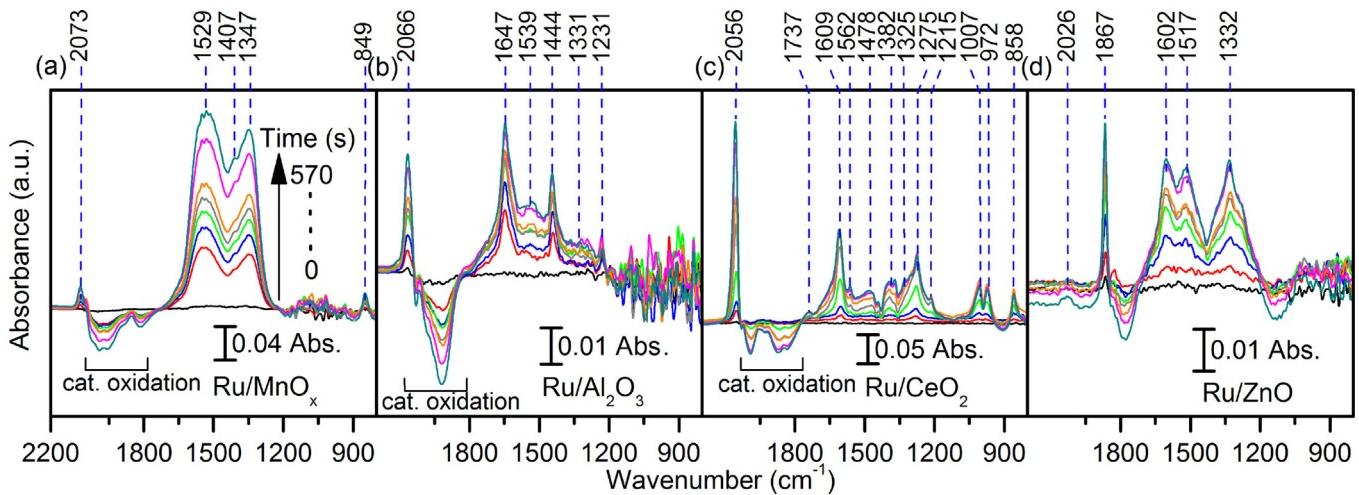


Fig. 13. Time-resolved DRIFT spectra of (a) Ru/MnO_x, (b) Ru/Al₂O₃, (c) Ru/CeO₂ and (d) Ru/ZnO, upon the introduction of 1% CO₂/He at 250 °C. The samples were pretreated at 350 °C with 10% H₂/He (Ru/ZnO pure He) for 10 min and cooled to 250 °C under He flow.

3.4. Reaction mechanism of CO₂ methanation

It is well established that the dissociative adsorption of CO₂ resulting in CO* on Ru is the first reaction step of CO₂ methanation [16,18]. The CO* is either further dissociated directly to form C* and O* followed by hydrogenation to CH_x*⁺, or it dissociates with the assistance of H* to form the hydroxylmethylene intermediate (HCOH*) followed by abstraction of O to form CH_x*⁺ [16,20–23]. In both case, the catalytic reaction rate depends on the ease of C–O bond breaking and the ratio of co-adsorbed CO* and H*. The measured amounts of chemisorbed H₂ and CO (Table 2) and the observed red shift of the carbonyl peak (Fig. 14d) indicate

that Ru/Al₂O₃ exhibits the highest Ru-CO coverage followed by Ru/CeO₂, Ru/MnO_x, and Ru/ZnO. The change in Ru-CO surface coverage hereby agrees with the support reducibility (Fig. 2). The reduced Ru-CO coverage can be explained by the reported weaker electron back-donation from precious metals to the π* orbital of CO and consequently weaker Ru-CO adsorption strength upon oxide support reduction [69,70]. Even though the C–O bond strength was not measured directly in this study, a change in the back-donation is expected to also alter the C–O bond. The reduction of the oxide support would cause a lower electron density in the anti-bonding π* orbital of CO, which would translate into a stronger C–O bond. Based on the above considerations it is expected that slightly

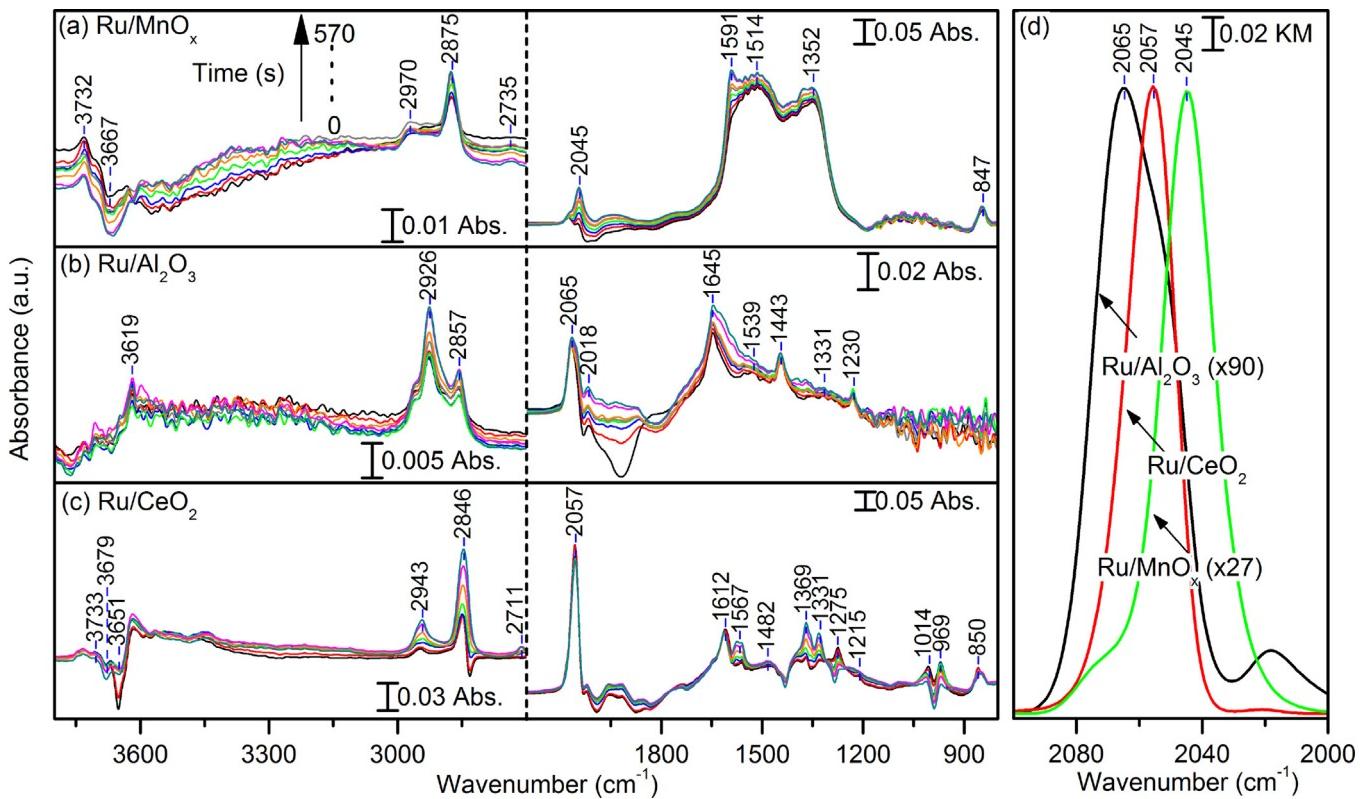


Fig. 14. Time-resolved DRIFT spectra of (a) Ru/MnO_x, (b) Ru/Al₂O₃ and (c) Ru/CeO₂, upon the introduction of 3.2% H₂ into the 1% CO₂/He at 250 °C. Shown in (d) is the corresponding carbonyl region for Ru/MnO_x, Ru/Al₂O₃ and Ru/CeO₂.

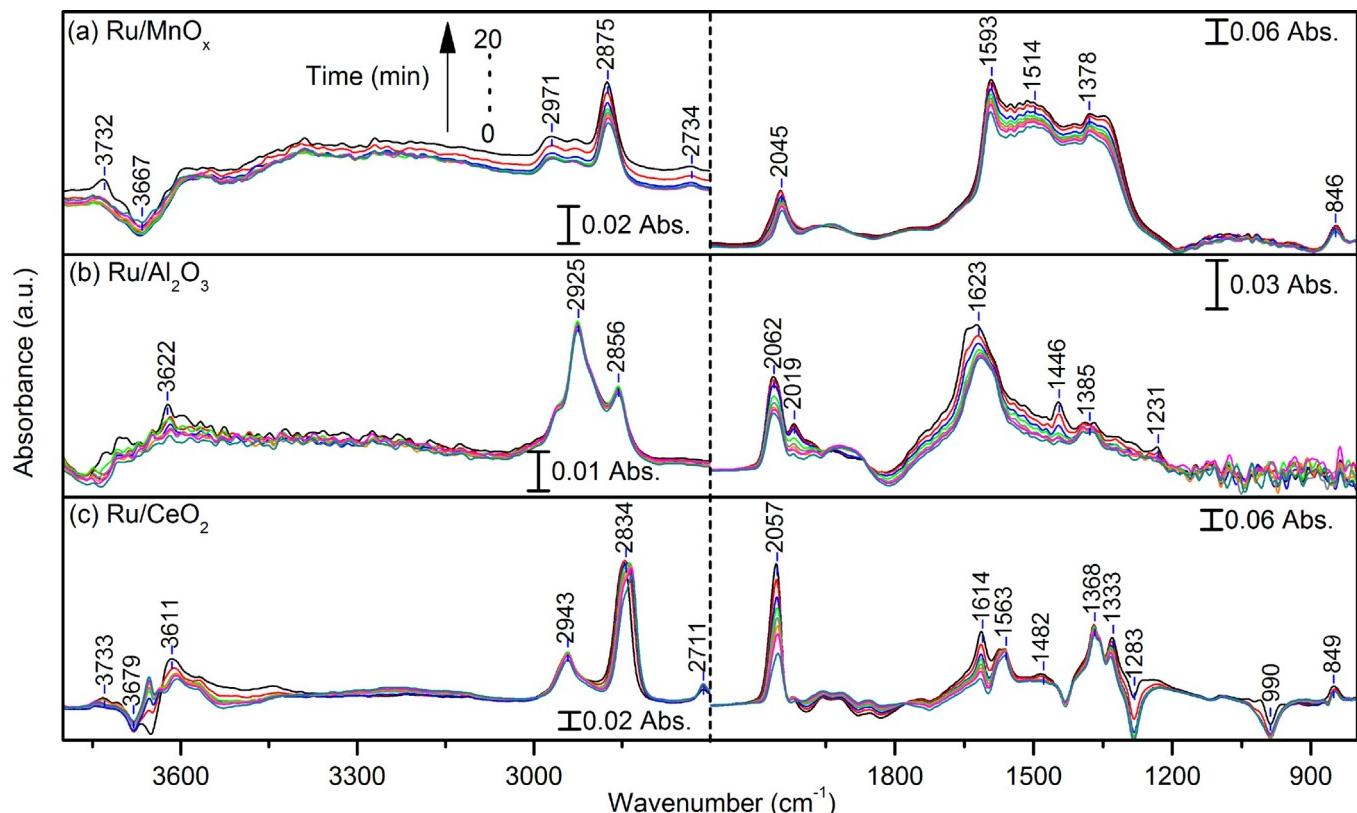


Fig. 15. Time-resolved DRIFT spectra of (a) Ru/MnO_x, (b) Ru/Al₂O₃ and (c) Ru/CeO₂, upon the removing of CO₂ from the preceding gas mixture of 1% CO₂/3.2% H₂/He at 250 °C.

reducible support resulting in an increased number of H₂ dissociation sites on Ru due to weaker CO adsorption but still sufficiently weak C–O bonds would result in the highest catalytic activity. CeO₂ is such a support and an excellent CO₂ conversion and CH₄ selectivity was observed for the Ru/CeO₂ catalyst (Fig. 8).

4. Conclusions

Flame spray pyrolysis was used for the synthesis of supported Ru nanoparticles and the influence of the metal oxide support on the catalytic methanation of CO₂ was investigated. The catalytic activity of the pristine oxide supports (Al₂O₃, CeO₂, MnO_x, and ZnO) was directly linked to the strength of basic sites, which resulted in large amounts of CO formed through the reverse water-gas shift reaction. However, no significant CH₄ formation was observed due to the absence of H₂ dissociation sites. The addition of Ru provided such sites and resulted in a high CO₂ conversion at low temperatures with CH₄ selectivities up to 95–100%. A thorough reaction kinetic analysis combined with quantitative gas chemisorption and *in situ* DRIFTS revealed that an enhanced support reducibility decreased the Ru-CO coverage. The reduced CO coverage increased the number of H₂ dissociation sites but in turn is expected to strengthened the C–O bonds due to a lower electron density in the π* antibonding orbital of CO. Hence, the CO₂ methanation on supported Ru requires a delicate tuning of the Ru-CO adsorption strength to obtain sites for H₂ dissociation while avoiding excessive strengthening of the C–O bond.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.08.011>.

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